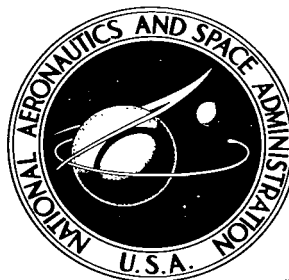


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# METALLURGICAL BONDING OF PLASMA-SPRAYED TUNGSTEN ON HOT MOLYBDENUM SUBSTRATES

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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# METALLURGICAL BONDING OF PLASMA-SPRAYED

## TUNGSTEN ON HOT MOLYBDENUM SUBSTRATES\*

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### SUMMARY

Metallurgically bonded plasma-sprayed tungsten was applied to metallographically polished and preheated molybdenum substrates. The substrates were preheated to 1750° F or higher immediately before spraying. The preheating and the spraying operations were performed in a nitrogen atmosphere.

Metallurgical bonding occurred when the preheated substrate temperature was between 2200° and 3700° F. At these temperatures the molybdenum substrates completely recrystallized even though the total time for preheating, spraying, and cooling to 400° F was only about 30 seconds.

Cross sections of coating and substrate indicate that the coating-to-substrate bond was the result of substrate grains growing into the coating.

### INTRODUCTION

The relation between the performance of a coating-substrate system and the quality of the bond between them is well known and has been studied extensively for many coating techniques. Little attention, however, has been given to the characterization of the bonding mechanisms that exist during plasma spraying and to the improvement of the quality of the bonding of coatings applied by this technique. In a previous investigation the authors reported the establishment of a true metallurgical bond and complete continuity of grain structure between plasma-sprayed tungsten and hot tungsten substrates (ref. 1). Since this type of bond occurred in a system where the lattice parameters of the sprayed particles and the substrate were equal, the system may be considered to be an ideal case. An effort was therefore made to determine the applicability of the original technique to dissimilar metal systems.

This report gives the results of spraying tungsten onto hot molybdenum substrates. These materials were selected because they are of interest to the aerospace program and because they form a complete series of solid-solution alloys. The main effort was directed toward determining whether this system would also exhibit metallurgical bonding by continuation of the substrate

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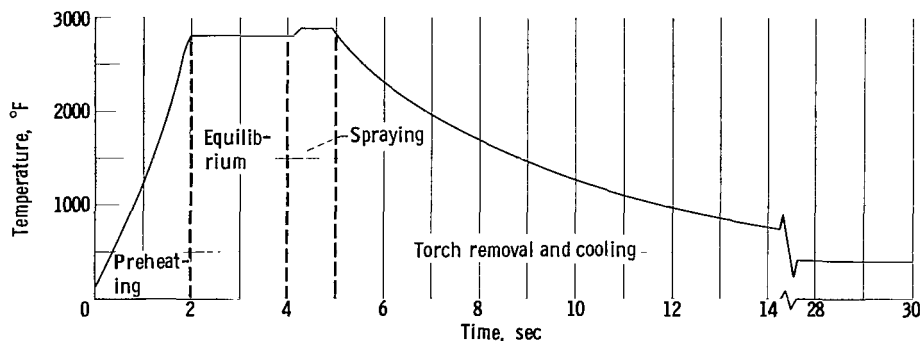


Figure 1. - Typical time-temperature history of substrate during spray treatment.

grains and by concurrent elimination of the coating-substrate interface as occurred in the tungsten-tungsten system.

### APPARATUS AND PROCEDURE

Small coupons of as-received 0.020-inch-molybdenum sheet were metallographically polished and subsequently plasma sprayed with tungsten powder in a high-purity dry-nitrogen atmosphere by techniques developed in an earlier investigation (ref. 1). Substrate temperatures in the range 1750° to 2950° F were continuously monitored by platinum - platinum-13-percent-rhodium thermocouples and read out on a millisecond response recorder. A typical spray cycle is shown in figure 1.

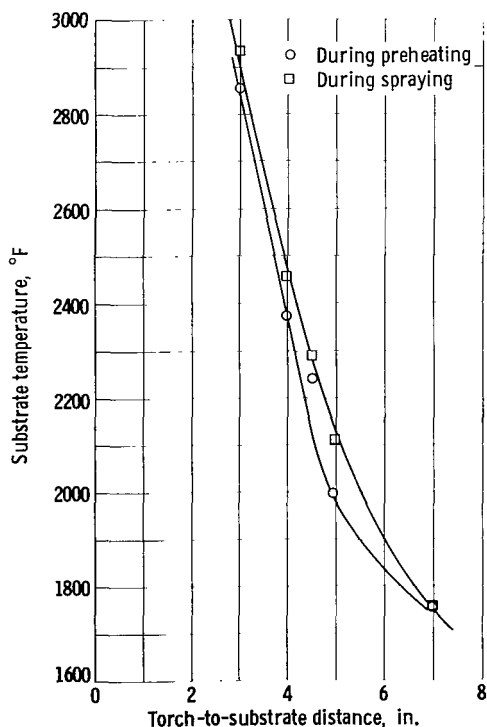


Figure 2. - Variation of substrate temperature with torch-to-substrate distance.

### RESULTS AND DISCUSSION

The substrate temperatures that were obtained as a result of preheating the specimens with the plasma gas varied with torch-to-substrate distance as shown in figure 2. This figure also shows the temperature of the substrate during the actual spraying operation. The velocity of the powder particles was nearly constant over the range of distances examined in this investigation (ref. 2).

For the torch-to-substrate distances investigated (2 to 7 in.), the tungsten particles exhibited a considerable amount of plasticity. This characteristic was demonstrated by their ability to deform into shapes similar to flat, almost-circular disks that had sufficient plasticity to flow over the previously deposited particles. A typical sprayed particle configuration on the substrate for a

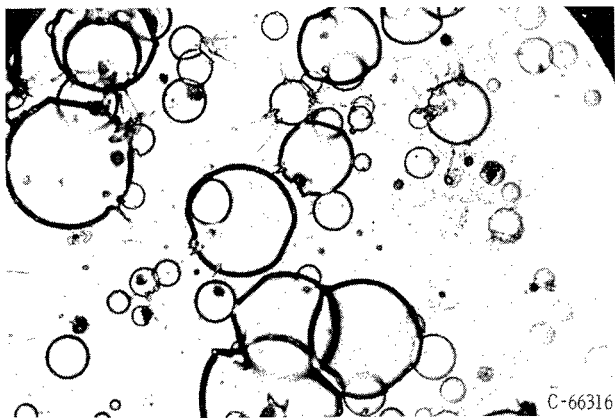


Figure 3. - Top view of particles. Torch-to-substrate distance, 4 inches; substrate temperature,  $\sim 2450^{\circ}\text{F}$ ; etchant, Murakami's reagent. X125.



(a) Torch-to-substrate distance, 3 inches; substrate temperature,  $\sim 2950^{\circ}\text{F}$ . X250.



(b) Torch-to-substrate distance, 4 inches; substrate temperature,  $\sim 2450^{\circ}\text{F}$ . X250.

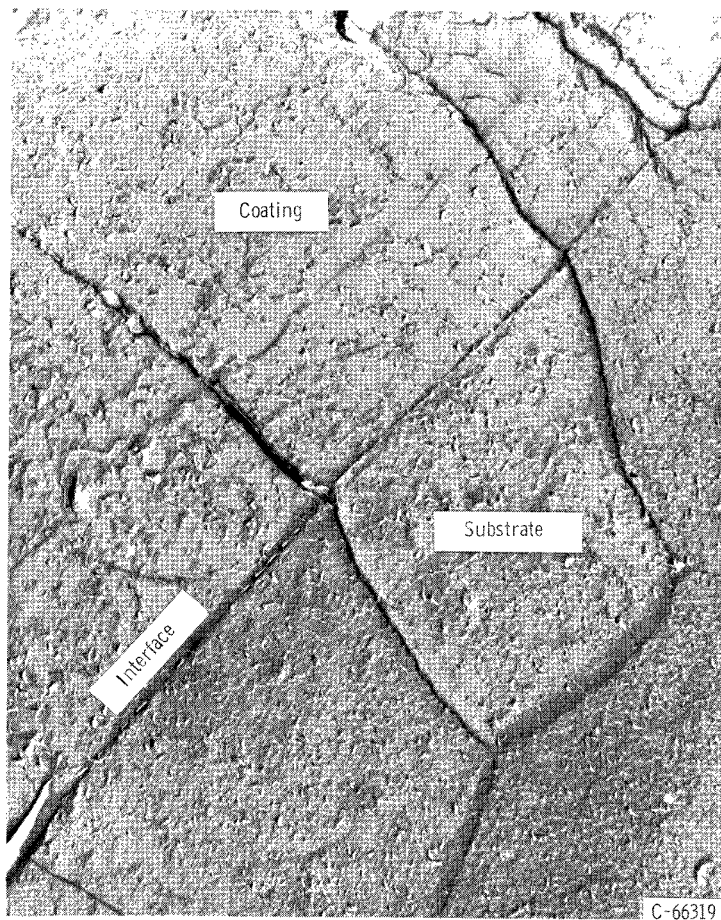
Figure 4. - Cross-sectional views of coating-substrate interfaces. Etchant, Murakami's reagent.

4-inch torch-to-substrate distance is shown in figure 3. Similar configurations were observed at the other spray distances.

The particle-substrate bonds resulting from spraying at torch-to-substrate distances of 3 and 4 inches are shown in figure 4 by cross sections through the coating and the substrate. Figure 4(c) is an electron micrograph at a magnification of 5000 for the 4-inch spray distance. The molybdenum substrates recrystallized as a result of preheating and spraying at distances up to 5 inches even though the total time for preheating, spraying, and cooling to  $400^{\circ}\text{F}$  was only about 30 seconds. At 7 inches the as-worked structure was retained. Spraying at distances of 5 and 7 inches resulted in a poorer particle-substrate bond. It therefore appears that the substrate must be preheated to a temperature of  $2200^{\circ}\text{F}$  or higher before good particle-substrate bonding occurs.

Grain-boundary continuity across the coating-substrate interface is evident in figure 4 and is most apparent in figure 4(c). Figure 5 shows an area where a continuity of etch markings exists across the interface, which gives evidence of an orientation continuity between the coating and the substrate. From these figures it is apparent that there is a metallurgical bond at the coating-substrate interface.

These observations on coating-substrate grain continuity are similar to those made when tungsten was deposited on hot tungsten substrates with the same spray conditions (ref. 1). A representative picture of the coating-substrate cross section for tungsten on tungsten is shown in figure 6. It is



(c) Torch-to-substrate distance, 4 inches; substrate temperature,  $\sim 2450^{\circ}\text{F}$ . X5000.  
Figure 4. - Concluded. Cross-sectional views of coating-substrate interfaces. Etchant, Murakami's reagent.

sprayed at a distance of 2 inches. The substrate temperature at this distance was estimated to be approximately  $3700^{\circ}\text{F}$ . A cross section of this specimen appears in figure 7 and shows the grain-boundary continuity across the inter-



Figure 5. - Effect of etching on interface structure. Torch-to-substrate distance, 3 inches; substrate temperature,  $\sim 2950^{\circ}\text{F}$ ; etchant, boiling Murakami's reagent. X500.

apparent not only that there is a continuity between the grains in the coating and those in the substrate but also that the original interface between them has been eliminated. Since molybdenum is very similar to tungsten, it was felt that the same type of interface should prevail in this system. Further experiments were therefore undertaken to show that the coating-substrate interface obtained when tungsten was sprayed onto hot molybdenum resulted from the chemical differences between the two materials at the interface.

Two approaches were taken to verify that the interface resulted from a chemical discontinuity. These approaches involved the use of a higher substrate temperature and diffusion treatments.

In order to evaluate the influence of a higher substrate temperature on the elimination of the apparent coating-substrate interface, an additional specimen was sprayed at 3 inches and subsequently vacuum heat treated at  $2700^{\circ}\text{F}$  for 3 hours and at  $3700^{\circ}\text{F}$  for 1 hour. After the  $2700^{\circ}\text{F}$  treatment there was no significant observable change in the interface discontinuity. After the subsequent  $3700^{\circ}\text{F}$  treatment,

Figure 8 shows a specimen that was sprayed at 3 inches and subsequently vacuum heat treated at  $2700^{\circ}\text{F}$  for 3 hours and at  $3700^{\circ}\text{F}$  for 1 hour. After the  $2700^{\circ}\text{F}$  treatment there was no significant observable change in the interface discontinuity. After the subsequent  $3700^{\circ}\text{F}$  treatment,

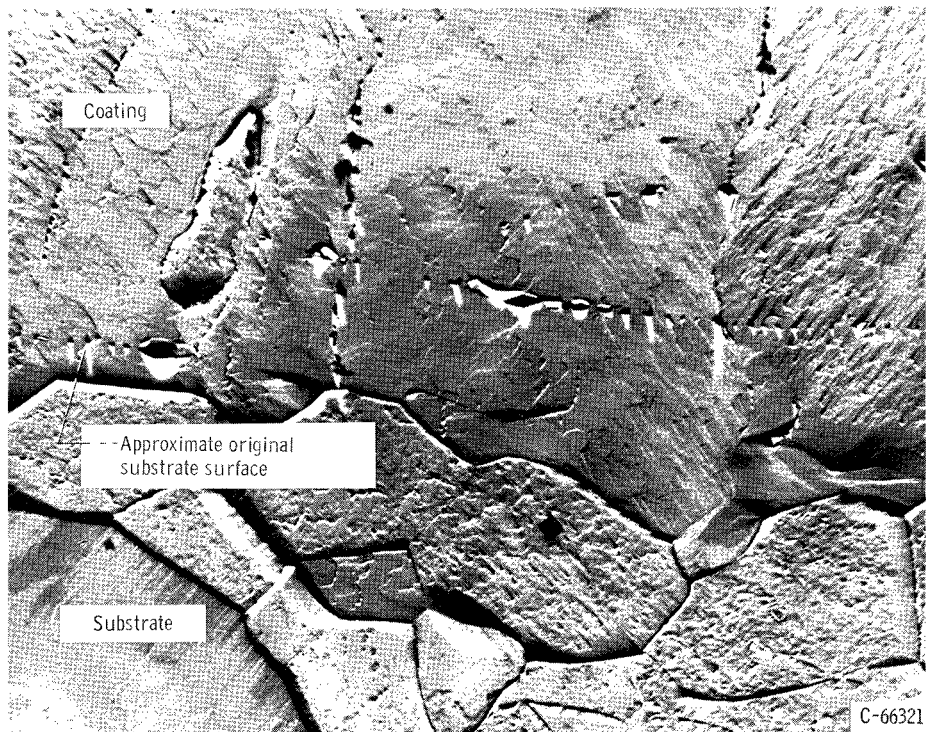


Figure 6. - Cross-sectional view of tungsten coating on tungsten substrate. Torch-to-substrate distance, 4 inches; substrate temperature,  $\sim 2750^{\circ}\text{F}$ ; etchant, Murakami's reagent. X5000.



Figure 7. - Cross-sectional view of interface of specimen sprayed at torch-to-substrate distance of 2 inches. Substrate temperature,  $\sim 3700^{\circ}\text{F}$ ; etchant, Murakami's reagent. X250.

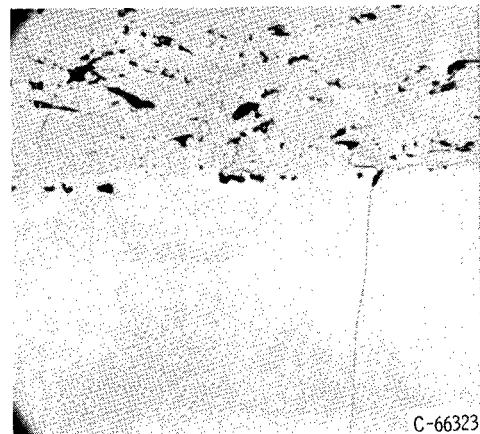


Figure 8. - Effect of diffusion treatment on interface structure. Torch-to-substrate distance, 3 inches; substrate temperature,  $\sim 2950^{\circ}\text{F}$ ; specimen heat treated at  $2700^{\circ}\text{F}$  for 3 hours and at  $3700^{\circ}\text{F}$  for 1 hour; etchant, Murakami's reagent. X250.

however, the apparent coating-substrate interface had been largely removed (fig. 8).

Figure 9 is a hardness traverse across the coating-substrate interface; it further substantiates that the heat treatment caused diffusion to occur, as

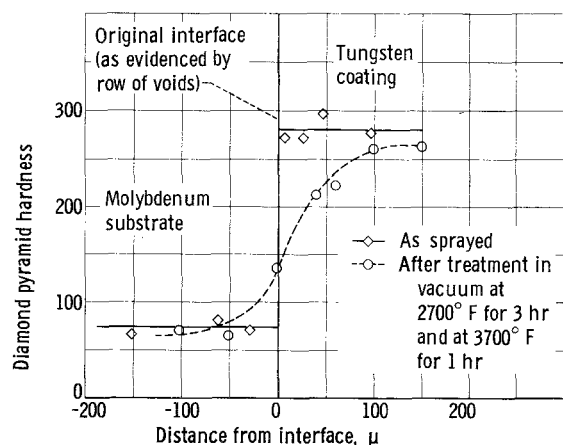


Figure 9. - Hardness as function of distance from original interface. Torch-to-substrate distance, 3 inches.

evidenced by the elimination of the original hardness discontinuity at the interface. It has been shown that the hardness of molybdenum is increased considerably by the addition of tungsten, whereas molybdenum additions to tungsten cause a decrease in the hardness of tungsten (refs. 3 and 4). The continuous-hardness change across the reference interface after the diffusion treatment is therefore verification that a significant amount of molybdenum diffused into the original tungsten particle. Also, since the original interface was eliminated after this heat treatment (see fig. 8), it must have resulted from a sharp chemical gradient.

These results show that a metallurgical bond similar to that obtained when tungsten is sprayed onto hot tungsten is obtained during the spraying of tungsten onto hot molybdenum substrates. This bond is produced by the grains of the coating growing out of those in the substrate, and the apparent interface that results is due to the sharp chemical gradient that exists between the tungsten and the molybdenum.

#### SUMMARY OF RESULTS

The following results were obtained from an investigation of the metallurgical bonding of plasma-sprayed tungsten on hot molybdenum substrates:

1. Metallurgically bonded tungsten coatings were applied to metallographically polished molybdenum substrates by plasma spraying with the substrate preheated to 2200° F or higher immediately before spraying in a nitrogen atmosphere.

2. The type of columnar grains that appeared in cross sections indicated that the coating-to-substrate bond was the result of substrate grains growing into the coating and thus producing a coherent interface. This apparent interface was due to a chemical gradient only, which was eliminated by heat treatment.

3. The substrates that were preheated over the temperature range 2200°



to 3700° F were completely recrystallized even though the total time for pre-heating, spraying, and cooling to 400° F was only about 30 seconds.

Lewis Research Center

National Aeronautics and Space Administration  
Cleveland, Ohio, April 7, 1964

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